Atom clusters and vibrational excitations in chemically-disordered $Pt_3{}^{57}Fe$

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Inelastic nuclear resonant scattering spectra of ^{57}Fe atoms were measured on crystalline alloys of $Pt_3{}^{57}Fe$ that were chemically disordered, partially ordered, and $L1_2$ ordered. Phonon partial density of states curves for ^{57}Fe were obtained from these spectra. Upon disordering, about 10% of the spectral intensity underwent a distinct shift from 25 to 19 meV. This change in optical modes accounted for most of the change of the vibrational entropy of disordering contributed by Fe atoms, which was $(+0.10 \pm 0.03)\ k_B\,(\text{Fe atom})^{-1}$. Prospects for parametrizing the vibrational entropy with low-order cluster variables were assessed. To calculate the difference in vibrational entropy of the disordered and ordered alloys, the clusters must be large enough to account for the abundances of several of the atom configurations of the first-nearest-neighbor shell about the ^{57}Fe atoms.

I. INTRODUCTION

Experimental and theoretical investigations have shown that changes in vibrational entropy can be important for the thermodynamics of solid-state phase transitions.[1–9] The recent emphasis of this work has been on how differences in vibrational entropy originate from differences in the phonon density of states (DOS) of the different phases. For example, there is experimental evidence that with chemical disorder, intensity in the optical modes is transferred to lower energies in the alloys Ni_3Al (Refs. 2,3) and Fe_3Al.[1,4,9] This trend would increase the vibrational entropy of the disordered alloy. On the other hand, theoretical calculations of the phonon DOS in ordered and disordered Ni_3Al show primarily a broadening of the optical modes[6,7] or even an increase in their average energy.[10] An open question about these *ab initio* calculations of interatomic forces is the minimum size of periodic calculational cell needed for reliable results.

Successful calculation of thermodynamic ground state functions such as configurational entropy and electronic energy by cluster expansion methods[11–13] is encouraging the use of these methods for obtaining the vibrational entropy. In cluster formalism[12,13] the part of the vibrational entropy contributed from the vibrations of Fe atoms, $S_{\text{vib}}^{\text{Fe}}$, is

$$S_{\text{vib}}^{\text{Fe}} = S_0^{\text{Fe}} + \sum_i S_i^{\text{Fe}} s_i + \sum_{j<i} S_{ij}^{\text{Fe}} s_i s_j + \sum_{k<j<i} S_{ijk}^{\text{Fe}} s_i s_j s_k + \cdots, \tag{1}$$

where the occupancy variables (or generalized spin variables) s_i and s_j are $+1$ when the site is occupied by a Pt atom and -1 when it is occupied by an Fe atom. As discussed below, this partial entropy $S_{\text{vib}}^{\text{Fe}}$ is related to the phonon partial DOS of Fe, $g^{\text{Fe}}(\varepsilon)$, which was measured in the present investigation. Here $g^{\text{Fe}}(\varepsilon)$ is

$$g^{\text{Fe}}(\varepsilon) = \left\langle \sum_j \left| \boldsymbol{\sigma}_j^{\text{Fe}}(\boldsymbol{q}) \right|^2 \delta(\varepsilon - \varepsilon_j) \right\rangle, \tag{2}$$

where $\boldsymbol{\sigma}_j^{\text{Fe}}$ is the polarization vector of an Fe atom for the jth vibrational mode. The average $\langle\rangle$ is over all Fe atoms.

A central and open question about the cluster expansion method is the number of terms in Eq. (1) that are required for reliable calculations of vibrational entropy. It is usually not possible to draw a correspondence between experimental data on $g^{\text{Fe}}(\varepsilon)$ and the cluster interactions $\{S_{ij\ldots}^{\text{Fe}}\}$. The present paper, however, reports a simple change in $g^{\text{Fe}}(\varepsilon)$ between disordered and $L1_2$-ordered Pt_3Fe. The change can be understood in terms of how chemical short-range disorder alters the vibrational modes of Fe atoms, which are local modes in the ordered alloy. By associating the important changes in atom vibrations with chemical environments, it is possible to deduce a lower bound on how many terms are required in Eq. (1) if it is to predict reliably the vibrational entropy of disordering.

II. EXPERIMENT

The present experiment was optimized for measuring spectra of optical modes. From coherent inelastic neutron scattering measurements on single crystals of $L1_2$-ordered Pt_3Fe,[16] it is known that the optical modes involve primarily the motion of Fe atoms, which are the species of low mass. The Fe atoms play a role in the lattice dynamics of $L1_2$ Pt_3Fe analogous to that of Al atoms in $L1_2$ Ni_3Al, and the local configurations of atoms around the Fe atoms undergo large changes between ordered and disordered states. The phonon partial DOS of ^{57}Fe was measured with the new technique of inelastic nuclear resonant scattering.[14,15] The measurements were performed at the 3-ID undulator beamline (SRI-CAT) of the Advanced Photon Source. A premonochromator consisting of water-cooled diamond (111) crystals in a nondispersive setting produced a beam of 14.413 keV synchrotron radiation with an energy bandwidth of 1.2 eV. Final monochromatization to an 875 μeV bandwidth with a photon flux of 6×10^8 Hz was provided by a high-resolution monochromator,[17] comprising two asym-

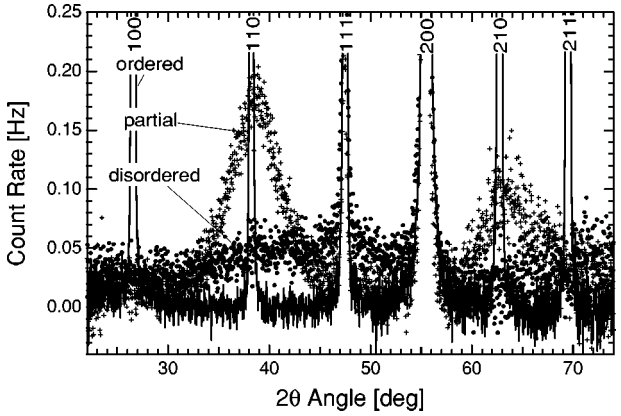

FIG. 1. X-ray diffraction pattern (Co $K\alpha$ radiation, Debye-Scherrer optics) from the three specimens of $Pt_3{}^{57}Fe$. Patterns were normalized by incident flux. Partially ordered and disordered samples received identical corrections for air scattering, background, absorption, and radiation polarization. The count rate for the (110) superlattice diffraction of the ordered sample exceeds 5 Hz.

metrically cut silicon (975) crystals in a dispersive geometry, and tuned in energy steps of 300 μeV. An avalanche photodiode with an active area of 2 cm^2 was mounted 4 mm above the specimen and was used for the detection of time-delayed *K*-shell internal conversion x rays of 6.4 keV.

Measurements were performed on three foils of $Pt_3{}^{57}Fe$ of 3 μm thickness at room temperature. The procedures for sample preparation were developed through extensive practice with Pt_3Fe materials containing natural Fe. Samples were prepared by arc melting a 220 mg ingot under an argon atmosphere, followed by piston-anvil quenching into a thin foil, cold rolling, and annealing in vacuum. One specimen of $Pt_3{}^{57}Fe$ was used directly after cold rolling, and is denoted the ''disordered'' sample. A second foil of $Pt_3{}^{57}Fe$ was annealed at 473 K for 1 h to induce partial chemical order, and is denoted the ''partially ordered'' sample. The third foil of $Pt_3{}^{57}Fe$, the ''ordered'' sample, was heated to 1173 K, cooled to 997 K over 5 h, and cooled to 300 K over 2 h. Differential scanning calorimetry measurements on disordered samples of Pt_3Fe using a Perkin Elmer DSC-4 showed a broad exothermic peak from 423 to 723 K that we associate with chemical ordering, although a previous report was more ambiguous.[18] From x-ray diffractometry, only the ''ordered'' sample showed significant $L1_2$ long-range order, as evidenced by intense x-ray superlattice diffractions of the (100) family (Fig. 1). The broad intensity from 33° to 44° in Fig. 1 for the partially ordered sample indicates a domain size of about 1.5 nm. The diffuse scattering from the disordered sample shows broad and weak variations in intensity, consistent with a first-nearest-neighbor (1NN) Warren-Cowley short-range-order (SRO) parameter of 0.1 or so. Such SRO will have only a small effect on the discussion below, in which the disordered sample is assumed to be a random solid solution. Quantitative determinations of chemical order were impaired by the rolling texture of the samples, however.

Conversion electron Mössbauer spectrometry is sensitive to local magnetic order. Previous work has shown that Pt_3Fe with $L1_2$ chemical order has a paramagnetic Mössbauer spectrum at room temperature, but the alloy and its spectrum

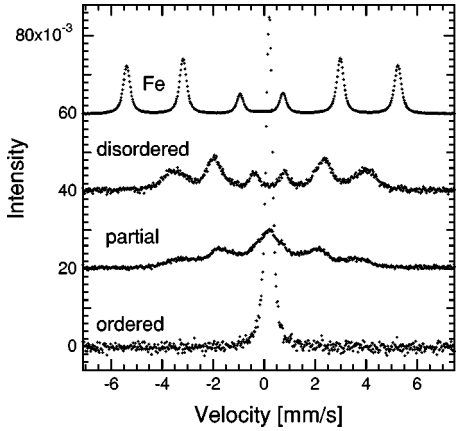

FIG. 2. Conversion electron Mössbauer spectra from bcc ^{57}Fe and the three specimens of $Pt_3{}^{57}Fe$, normalized by area.

become partially ferromagnetic after plastic deformation.[19,20] The partially-ordered sample has a Mössbauer spectrum intermediate between the fully paramagnetic spectrum of the ordered sample and the fully ferromagnetic spectrum of the disordered sample (Fig. 2). These spectra show that the disordered sample is chemically disordered over the characteristic magnetic screening length.

III. RESULTS

Inelastic nuclear resonant scattering spectra are presented in Fig. 3. The Mössbauer elastic peak at $\varepsilon = 0$ meV is

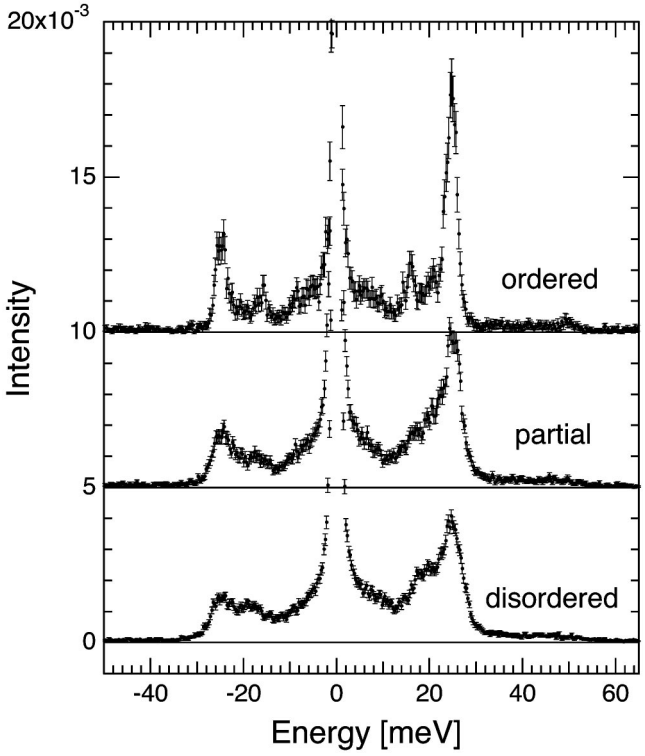

FIG. 3. Conversion x-ray intensity versus photon energy from the disordered, partially ordered, and ordered alloys near the elastic (Mössbauer) resonance set at 0 meV. Spectra are normalized for equal intensities of inelastic scattering. Curves for the partially ordered and ordered samples are shifted vertically.

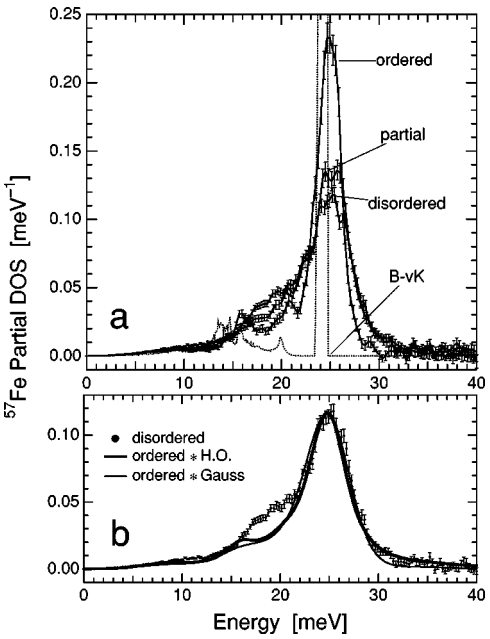

FIG. 4. Phonon partial DOS curves for ^{57}Fe in $Pt_3{}^{57}Fe$. (a) Experimental phonon partial DOS curves obtained from the spectra of Fig. 3, and curve calculated from a Born–von Kármán model. All curves normalized to 1. B-vK curve extends to 1.8. (b) Disordered phonon partial DOS curve for ^{57}Fe in disordered $Pt_3{}^{57}Fe$, together with curves calculated by convolution of the ordered curve with a Gaussian function of $\sigma = 2.6$ meV (ordered * Gauss), and a damped harmonic oscillator function with $Q = 12$ (ordered * H.O.). Normalizations were chosen to provide best fits around 25 meV.

surrounded by the inelastic contribution from nuclear resonant photon absorption accompanied by phonon creation (right) and phonon annihilation (left). Vibrational modes around 25 meV exist in the disordered alloy, but show a systematic growth in intensity and sharpness with chemical order. A feature around 16 meV becomes sharper with increasing order, but the intensity from 10 to 20 meV actually becomes weaker with respect to the modes at 25 meV. The intensity from 30 to 55 meV is primarily two-phonon scattering.[21] In the ordered alloy, a peak in the two-phonon scattering is observed at 50 meV, which is the sum of two 25 meV excitations. We corrected for the multiphonon scattering by a Fourier-logarithm deconvolution method described previously.[15,22]

With interatomic force constants from prior measurements of dispersion curves on single crystals by Noda and Endoh,[16] a Born–von Kármán lattice dynamics calculation was performed for $L1_2$-ordered Pt_3Fe. The dynamical matrix was diagonalized for about 10^7 values of $\mathbf{k}$ in the first Brillouin zone, and histogram binning of the eigenfrequencies was used to obtain the phonon DOS, $g(\varepsilon)$. The dispersion curves for the optical modes were quite flat, and the DOS had a sharp peak at 24–25 meV. For each eigenmode j two other histograms were prepared with weights provided by the square of the polarization vectors, $|\boldsymbol{\sigma}_j^{\mathrm{Fe}}(\boldsymbol{q})|^2$ and $|\boldsymbol{\sigma}_j^{\mathrm{Pt}}(\boldsymbol{q})|^2$, so the phonon partial DOS curves were obtained for the Fe and Pt atoms as in Eq. (2). The result for $g^{\mathrm{Fe}}(\varepsilon)$ is labeled B-vK in Fig. 4(a). The main peak of this B-vK DOS is about 0.6 meV lower in energy than our measured peak for the ordered alloy, but we consider this a reasonable agreement.

Figure 4(a) presents the phonon partial DOS curves of ^{57}Fe from samples of $Pt_3{}^{57}Fe$ with different states of chemical order. The optical modes at 25 meV are broadened with disorder, much as has been calculated or measured previously for transition metal aluminides.[3,6–10] A broadening that is symmetrical in energy has little effect on the vibrational entropy, however. Of greater significance are the decrease in intensity around 25 meV and the increase in intensity around 19 meV. This trend is presented more clearly in Fig. 4(b), which compares the experimental phonon partial DOS of the disordered alloy to the curve of the ordered alloy after broadening by convolution with a Gaussian function or a damped harmonic oscillator function[23,24] (which is much like a Lorentzian function). By integrating the curves in Fig. 4(b), it is found that with disorder a total of 12% of the intensity is transferred out of the peak at 25 meV. Most of this transfer, 10%, appears as intensity around 19 meV. The breadth of the new intensity around 19 meV is approximately the same as the breadth of the intensity around 25 meV. Any interpretation of the effects of disorder on the phonon DOS must at least explain the systematic shift of intensity from 25 to 19 meV.

IV. DISCUSSION

A. Vibrations of atom clusters

Since the optical modes are almost dispersionless in $L1_2$-ordered Pt_3Fe, the vibrations of Fe atoms are described reasonably well as localized Einstein modes. In ordered Pt_3Fe, each Fe atom vibrates within a cage of 12 1NN Pt atoms that are 3.5 times as massive as Fe atoms. The 1NN Pt-Pt force constants are larger than 1NN Pt-Fe force constants.[16] As for other ordered alloys,[25,26] this difference in force constants is consistent with Pt having a larger metallic radius (0.139 nm) than Fe (0.127 nm).[27] We performed similar lattice dynamics calculations on bcc Fe and fcc Pt using published force constants.[28,29] Compared to bcc Fe, the mean and variance of the phonon partial DOS of Fe atoms decrease in $L1_2$ Pt_3Fe by 15% and 52%, respectively. This big change of the Fe DOS can be associated with the larger average 1NN interatomic separation in Pt_3Fe (0.272 nm) than in bcc Fe (0.247 nm). On the other hand, compared to fcc Pt (with 1NN separation of 0.277 nm) the mean and variance of the phonon partial DOS of Pt atoms decrease in $L1_2$ Pt_3Fe by only 5% and 19%, respectively.

The change with disorder of the ^{57}Fe partial DOS can also be understood with a picture in which the majority Pt atoms serve as a rigid framework against which the Fe atoms vibrate in localized modes. Chemical disorder will create local environments where ^{57}Fe atoms have various numbers of 1NN Fe atoms (compared to zero 1NN Fe atoms in the $L1_2$ ordered structure). These Fe-rich configurations vandalize the stiffness of the Pt framework. Owing to the large interatomic spacing of Fe pairs in the fcc Pt-rich framework, we expect lower vibrational frequencies for ^{57}Fe atoms having many Fe neighbors. These altered vibrations may not be Einstein modes, but changes to cooperative modes will still be evident in the measured $g^{\mathrm{Fe}}(\varepsilon)$ of the disordered alloy.

If the Pt atoms serve as a framework of rigid spheres, the softening of vibrations of the ^{57}Fe atom requires at a minimum that 3 of its 12 1NN Pt atoms are replaced by Fe atoms.

The ^{57}Fe atom and these three 1NN Fe atoms form a tetrahedron, permitting a soft direction for the movement of the ^{57}Fe atom toward the center of the tetrahedron. In the fcc structure there are eight such 1NN tetrahedra about a central ^{57}Fe atom. One-third of the modes of a three-dimensional Einstein oscillator can be associated with this one direction. This model of physical 1NN tetrahedra therefore predicts that the fraction of tetrahedral clusters should be multiplied by 8/3 to obtain the fraction of affected intensity f in $g^{\mathrm{Fe}}(\varepsilon)$. For a tetrahedron of three Fe neighbors about the central ^{57}Fe atom, $f=1/24$, so 4% of the local environments would be affected in the disordered alloy. This is much smaller than the observed shift with disorder of 10% of the Fe partial DOS from 25 to 19 meV.

B. Parametrization of vibrations with general clusters

With our measured $g^{\mathrm{Fe}}(\varepsilon)$ we can identify the fraction of ^{57}Fe atoms that vibrate at lower frequencies owing to their altered Fe neighborhoods in the disordered alloy. For a disordered solid solution we know the probabilities that an ^{57}Fe atom will have various numbers of Fe first neighbors. In this section these probabilities are used to estimate the minimum level of detail on chemical short-range order required to parametrize the phonon partial DOS. This is done within the cluster framework of Eq. (1), where the clusters are used to parametrize the partial entropy. Since the change with disorder in partial entropy originates primarily with an explicit change in modes that were local modes of ^{57}Fe atoms in the ordered alloy, the clusters needed to parametrize the change in vibrational entropy should also be able to parametrize the change in the phonon partial DOS. (These generalized clusters need not provide a realistic picture of the vibrational dynamics of physical atom clusters, however.)

Each atom cluster that includes an ^{57}Fe atom makes a contribution to the partial entropy, $S_{\mathrm{vib}}^{\mathrm{Fe}}$ of Eq. (1), but the usage of Eq. (1) requires that we first account for all contributions from the subclusters of any cluster.[11,13] We therefore test in sequence the probabilities of all atom clusters in disordered and ordered alloys to find a bound on the lowest-order term in Eq. (1) that could parametrize an observed shift of 10% of the Fe partial DOS from 25 to 19 meV with disorder.

In $L1_2$-ordered Pt_3Fe the 1NN atoms about ^{57}Fe atoms are exclusively Pt, whereas in a disordered alloy the 1NN atoms of an ^{57}Fe atom are 3/4 Pt and 1/4 Fe. For our measurements on disordered Pt_3Fe, the interesting clusters of the disordered alloy will be Fe rich. Although the 1NN pair cluster of Eq. (1) may be responsible for some broadening of the spectrum, too many 1NN Fe-Fe pair clusters are present in the disordered alloy to account for a distinct shift of 10% of the spectral intensity.

We seek to parametrize the shift with disorder of 10% of the intensity in $g^{\mathrm{Fe}}(\varepsilon)$ from 25 to 19 meV by a 10% change of some local chemical environment(s). In a random Pt-Fe alloy of concentration $c=1/4$, the probability of finding n Fe atoms in a group of N 1NN sites about a ^{57}Fe atom, $p(N,n,1/4)$, is the binomial probability

$$p(N,n,1/4)=\frac{N!}{(N-n)!\,n!}\left(\frac{3}{4}\right)^{N-n}\left(\frac{1}{4}\right)^{n}. \tag{3}$$

To identify a possible origin for the shift with disorder of 10% of the spectral intensity of $g^{\mathrm{Fe}}(\varepsilon)$, we examined the binomial probabilities to find the smallest N for which $p(N,n,1/4)$ was approximately 0.1, or when the sum of $p(N,n,1/4)$ for a given N was approximately 0.1. For example, when $N=1$ the smallest value of $p(N,n,1/4)$ is $p(1,1,1/4)=1/4$, which is much larger than 0.1 as noted above when we considered the 1NN pair variables. The smallest acceptable value of N is 5, for which

$$p(5,4,1/4)+p(5,5,1/4)=\frac{105}{1024}\approx 0.1. \tag{4}$$

A configuration of the ^{57}Fe atom and five atoms in its 1NN shell does not have an obvious physical structure on the fcc lattice. The identification of this six-atom cluster indicates instead a minimum level of structural detail that must be known to account for the experimental observation of a shift of 10% of the intensity of $g^{\mathrm{Fe}}(\varepsilon)$ from 25 to 19 meV. To be reliable, a cluster approximation should provide at least enough structural information to account for the abundance of the Fe-rich six-atom clusters of neighboring atoms. Larger clusters, or more clusters, may be required, since the present analysis provides only a lower bound. The SQS-8 model[10] for disordered A_3B alloys does not satisfy this lower bound.

Many physical atom configurations can be used for cluster parametrizations, but the 13-atom configuration comprising the central ^{57}Fe atom and its 12 first neighbors is a natural choice. By examining binomial probabilities, we deduce that ^{57}Fe atoms having five or more Fe neighbors can parametrize the change in vibrational modes with disorder. (Note that $p(12,5,1/4)=0.1032$, $p(12,6,1/4)=0.0401$, and larger numbers of Fe atoms have a cumulative probability of less than 0.015.) Figure 4(a) shows that in the disordered alloy, most of the Fe partial DOS remains around 25 meV, even though the fraction of Fe atoms with zero Fe neighbors, $p(12,0,1/4)$, is only 0.0317. Those Fe atoms with one to four Fe neighbors could parametrize the broadening of the phonon partial DOS. (We cannot tell if a physical explanation of this broadening involves shifts in frequencies of local modes, or the development of a dispersion of cooperative modes.) Finally, we note that for the partially ordered sample, the intensity in the ^{57}Fe partial DOS at 19 meV is intermediate between those of the disordered and ordered samples. It is plausible that the SRO in the partially ordered sample could eliminate about half of the Fe-rich 1NN environments in the disordered alloy.

C. Partial entropy of Fe atoms

The total vibrational entropy, $S_{\mathrm{vib}}(T)$ is calculated from the total phonon DOS $g(\varepsilon)$ as

$$S_{\mathrm{vib}}(T)=-3\,k_B\int_0^{\infty} g(\varepsilon)[(n_\varepsilon+1)\ln(n_\varepsilon+1)-n_\varepsilon\ln(n_\varepsilon)]d\varepsilon, \tag{5}$$

where n_ε is the Bose-Einstein distribution at temperature T, and $g(\varepsilon)$ is the sum over all $3N$ phonon modes, each denoted j,

$$g^{\mathrm{Fe}}(\varepsilon)=\sum_{j}^{3N}\ \delta(\varepsilon-\varepsilon_j). \tag{6}$$

The polarization vectors as in Eq. (2) are normalized,

$$\tfrac{1}{4}\,|\boldsymbol{\sigma}^{\mathrm{Fe}}(\varepsilon_j)|^2+\tfrac{3}{4}\,|\boldsymbol{\sigma}^{\mathrm{Pt}}(\varepsilon_j)|^2=1. \tag{7}$$

Using Eqs. (7) and (6) in Eq. (5) we have

$$S_{\mathrm{vib}}(T)=\tfrac{1}{4}\,S^{\mathrm{Fe}}_{\mathrm{vib}}(T)+\tfrac{3}{4}\,S^{\mathrm{Pt}}_{\mathrm{vib}}(T), \tag{8}$$

where

$$S^{\mathrm{Fe}}_{\mathrm{vib}}(T)=-3\,k_B\int_0^{\infty}\sum_{j}^{3N}\ \delta(\varepsilon-\varepsilon_j)\,|\boldsymbol{\sigma}^{\mathrm{Fe}}(\varepsilon_j)|^2 \times[(n_\varepsilon+1)\ln(n_\varepsilon+1)-n_\varepsilon\ln(n_\varepsilon)]\ \ d\varepsilon, \tag{9}$$

$$S^{\mathrm{Fe}}_{\mathrm{vib}}(T)=-3\,k_B\int_0^{\infty}g^{\mathrm{Fe}}(\varepsilon) \times[(n_\varepsilon+1)\ln(n_\varepsilon+1)-n_\varepsilon\ln(n_\varepsilon)]\,d\varepsilon, \tag{10}$$

and

$$S^{\mathrm{Pt}}_{\mathrm{vib}}(T)=-3\,k_B\int_0^{\infty}g^{\mathrm{Pt}}(\varepsilon) \times[(n_\varepsilon+1)\ln(n_\varepsilon+1)-n_\varepsilon\ln(n_\varepsilon)]\,d\varepsilon. \tag{11}$$

At high temperatures Eq. (10) can be used to show that the partial entropy is related to the partial phonon DOS as

$$S^{\mathrm{Fe}}_{\mathrm{vib}}=-3k_B\int_0^{\infty}g^{\mathrm{Fe}}(\varepsilon)\ln(\varepsilon)\,d\varepsilon. \tag{12}$$

We evaluated the high-temperature limit of Eq. (12) with the $g^{\mathrm{Fe}}(\varepsilon)$ curves presented in Fig. 4(a), and found the contribution of the Fe atoms to the vibrational entropy to be larger in the disordered alloy by $(+0.10\pm0.03)\ k_B$ (Fe atom)$^{-1}$. The observed shift from 25 to 19 meV of the intensity in the phonon partial DOS of Fe provides a contribution to $S^{\mathrm{Fe}}_{\mathrm{vib}}$ of $3k_Bf\ln(25/19)=f\times0.82k_B$. The fraction of affected intensity, f, is approximately 0.1, so $S^{\mathrm{Fe}}_{\mathrm{vib}}\approx0.082\ k_B$ (Fe atom)$^{-1}$. Evidently this shift in optical modes with disordering accounts for most of the change in the partial entropy of the Fe atoms of $(+0.10\pm0.03)\ k_B$ (Fe atom)$^{-1}$.

V. CONCLUSIONS

Phonon partial density of states curves for ^{57}Fe were obtained from inelastic nuclear resonant scattering spectra from samples of $Pt_3{}^{57}Fe$ that were chemically disordered, partially ordered, and $L1_2$ ordered. There was some broadening of the features of the phonon partial DOS $g^{\mathrm{Fe}}(\varepsilon)$ upon disordering, but more relevant to the vibrational entropy was an observed shift of about 10% of the spectral intensity from 25 to 19 meV.

In $L1_2$-ordered Pt_3Fe, for which the lattice dynamics are known in detail, the $g^{\mathrm{Fe}}(\varepsilon)$ can be understood as the motions of Fe atoms within cages of massive 1NN Pt atoms, stiffly bonded to other Pt neighbors. The effect of chemical disorder is to replace some of these 1NN Pt atoms about the ^{57}Fe atoms by Fe neighbors, vandalizing the stiffness of the cage. We therefore expect Fe-rich neighborhoods to cause the observed shift in frequency of about 10% of the spectral intensity upon disordering from 25 to 19 meV. The probabilities of these Fe-rich environments in disordered alloys were used to identify the minimum number of Fe neighbors required to understand the vibrational entropy of disordering. To calculate the difference in vibrational entropy of the disordered and ordered alloys, the chemical order must be specified with at least sufficient detail to account for the abundances of several of the atom configurations of the 1NN shell.

The vibrational entropy can be expressed as the sum of vibrational contributions from the phonon partial DOS's of Pt and Fe atoms. The contribution of the Fe atoms to the vibrational entropy of disordering was $(+0.10\pm0.03)\ k_B$ (Fe atom)$^{-1}$.

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